Interfacial Tension Experimental Values and Correlation for n-alkane-Water

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ABSTRACT

Interfacial tension was measured experimentally for different liquid hydrocarbons-water systems (n-hexane, n-heptane, n-octane, n-nonane and n-dodecane) using the pendant drop experimental technique with a numerical method developed by López de Ramos *et al.*[1] The experimental equipment used to generate the pendant drop consists of a cell with a stainless steel body and two Pyrex windows. The inner cell was previously filled with water. A surgical needle (at the top of the cell) was used to introduce the organic phase into the cell (forming the pendant drop). Water was used to keep the temperature constant inside the cell (between 10 and 60 °C). The cell was illuminated from the back using a fiber optic lamp and a diffuser. A video camera (with a 60 mm micro lens and an extension ring) was located at the front window. The pendant drop image was captured and sent to the video recording system. The cell and the optical components were placed on an optical table with vibration isolation legs. A new correlation was found to predict interfacial tension (γ) as a function of temperature (T) and the number of atoms of carbon (n) with a deviation of less than 1% from experimental values.

KEY WORDS: Hydrocarbon/Water System, Interfacial Tension, Interfacial Tension and Temperature , Interfacial Tension Correlation.

1. INTRODUCTION

Many investigations are dealing with the characterization of water/oil interfaces because of its relevance in many industrial applications. Although in the literature several works can be found with organic/water systems, few of them use the innovative technique of the pendant drop.

The objective of this work was to calculate interfacial tension from the pendant drop experimental technique and the mathematical model developed by López de Ramos *et al.*[1] for n-alkane/water systems. Additionally, a new correlation for interfacial tension as a function of temperature and carbon atom number is proposed.

2. MATHEMATICAL MODEL

The shape of liquid drops (pending from a surface) can be described by the Laplace-Young equation. This equation is just a balance between gravity, hydrostatic pressure, and surface tension effects. When drops are axisymmetric, the Laplace-Young equation can be written as:

$$\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=-\frac{\Delta\rho g y}{\gamma}+f(R_0) \qquad (1)$$

where γ is the surface tension, R_1 and R_2 are the principal radii of curvature, $\Delta\rho$ is difference in densities of the two fluids, g is the gravitational acceleration and R_0 is the radius of curvature at y=0 (Fig. 1). The term $\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$ is the mean curvature of the drop,

this curvature is a function of the *y* position and can be expressed using differential geometry as:

$$\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\frac{d^2y/dx^2}{\left[1+(dy/dx)^2\right]^{3/2}}+\frac{dy/dx}{x\left[1+(dy/dx)^2\right]^{1/2}} \qquad (2)$$

Solutions to the Young-Laplace equation for pendant drop (Eq. (1)) predict a linearly varying curvature as a function of elevation. Plotting the mean curvature of the pendant drop versus elevation renders a straight line with slope $-\frac{\Delta\rho g y}{\gamma}$. Computer-generated spline functions were used to represent the experimental data to a prescribed degree of smoothness. In turn, derivatives of the spline functions provide an accurate and reliable way to determine the curvature (Eq. (2)) of the drop image.

3. EXPERIMENTAL METHODS

3.1. Chemicals

Several pendant drop experiments were made at atmospheric pressure. The organic phase used was hexane (99%, Aldrich), heptane (99%, Aldrich), octane (99%, Aldrich), nonane (99%, Aldrich) and dodecane (99+%, Aldrich). All organic liquids were distilled in all-glass apparatus to remove any-active impurities. Water was also distilled in all-glass apparatus (three times).

3.2. Equipment

In order to create pendant drops, a stainless steel cell was designed with two Pyrex windows. These windows are sealed to the cell body through a gasket (grafoil, 1/16 inch of

thickness). The liquid phase can be introduced into the cell from the top or from the bottom in order to create pendant or sessile drops. A surgical needle inserted at the top of the cell is used to form pendant drops. A small hole on the bottom surface allows the formation of emergent or captive drops. There is a thermocouple well in one of the sides. Four channels spanning the width of the cell are used to circulate water, keeping the temperature constant inside the cell. The circulating water temperature is controlled using a constant temperature bath. Figure 2 is a schematic view of the complete experimental set-up.

The cell is illuminated from the back using a fiber optic lamp. A diffuser is placed between the lamp and the rear window. A video camera (CCD-72 from DAGE-MTI Incorporated) is located at the front window. Two lenses can be attached to the video camera through a C connector. One of the lenses is the Nikkon 55 mm micro with a PK-13 extension ring and the other lens is the D. O. Industries Zoom 6000 Microscopic. The pendant drop image can be captured easily and it can be sent to the video recording system (Panasonic AG-7300) or to the computer (using the Targa® videographic system connected to Intel®80586-100 Mhz CPU with VGA card and monitor). The image visualization equipment is also furnished with a Sony PVM2530 RGB monitor. The cell and the optical components are placed on an optical tubular bench with vibration isolation legs. Figure 3 shows an original pendant drop image (in TARGA format). Figure 4(a) presents the black and white image and Fig. 4(b) shows the pendant drop outline. From the drop image outline the *xy* profile is obtained using a program in Visual-Basic. Finally, the interfacial tension can be calculated using a spline method.

3.3. Calibrations

The pendant drop technique used to determine interfacial tension does not really need any correction factors[2].

The mathematical method with the computational program was tested calculating the surface tension for an hypothetical water drop profile. This drop profile was generated from the Laplace-Young Equation using a theoretical surface tension value of 72.10 mN/m. After using the program, the value of surface tension obtained perfectly matched the theoretical value.

The experimental procedure was previously tested with excellent results[1,3]. The propagation errors calculations predict a value of $\Delta\gamma \approx \pm 0.04$ mN/m.

3.4. Procedures

After choosing the n-alkane/water system and having the inner cell filled with water, a surgical needle is used to introduce the organic phase into the cell (forming the pendant drop). The cell temperature is set between 10 and 60 ^{o}C. Then, the pendant drop image is recorded using the video system and the image capture procedure begins. The final result is the *xy* drop profile.

It is important to allow enough time to achieve stability at the interface. It is not the purpose of this work to compute dynamic interfacial tension.

3.5. Calculation of Interfacial Tension

With the *xy* profile and the computational program, the interfacial tension value is then calculated.

4. RESULTS AND DISCUSSION

On Table 1 are reported all the experimental interfacial tension values for all the n-alkanes/water systems selected. Figure 5 shows the interfacial tension values as a function of temperature for all the system studied. As it can be seen, there is a lineal dependence between γ and T. Table 2 presents all the lineal regression equations that fit the experimental data. As a carbon atom number increases, interfacial tension decreases. Table 3 compares the experimental values calculated using the lineal equation (Table 2) at 22^{o}C with those reported at the same temperature by Goebel and Lunkenheimer[4]. Although these values do not match perfectly, tendencies of interfacial tension values with the carbon atom number are the same. Theses differences could be caused by the no similarities in purity and quality of the chemicals used in both research works.

The correlation that best fit the experimental data has the form of:

$$\gamma = A.n^{B} \tag{3}$$

where A and B are calculated using the following equations:

$$\frac{A}{T} = -4.3x10^{-5}T^{3} + 5.885x10^{-3}T^{2} - 0.2934T + 6.1384 \tag{4}$$

$$\frac{B}{T^{2}} = -5.2x10^{-7}T^{3} + 7.011x10^{-7}T^{2} - 3.265x10^{-5}T + 5.596x10^{-4} \tag{5}$$

The maximum deviation presented, between correlation and experimental values, was 0.2%.

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LITERATURE CITED

(1) López de Ramos, A.; Redner, R.; Cerro,R. L. Surface Tension from Pendant Drop Curvature. Langmuir **1993**, 9, 3691-3694.

(2) Jenning, J.; Pallas, N. R. An Efficient Method for the Determination of Interfacial Tensions from Pendant Drop Profiles. Langmuir **1988**, 4, 4, 959-967.

(3) López de Ramos, A. Capillary Enhanced Diffusion of CO_2 in Porous Media; Doctor of Philosophy Dissertation, The University of Tulsa, 1993.

(4) Goebel, A.; Lunkenheimer, K. Interfacial Tension of the Water/n-Alkane Interface. Langmuir **1997**, 13, 2, 369-372.

Table 1. Interfacial tension experimental values at different temperatures (T)

	Interfacial tension, γ /mN.m^{-1} ± 0.04				
T/°C ± 0.1	n-hexane-water	n-heptane-water	n-octane-water	n-nonane-water	n-dodecane-water
10.0	51.43	-	52.27	52.69	53.54
15.0	51.11	-	52.01	52.37	53.20
20.0	50.80	51.24	51.64	52.06	52.87
25.0	50.38	50.71	51.16	51.63	52.55
27.5	50.11	50.47	51.00	51.48	52.34
30.0	49.96	50.30	50.74	51.21	52.14
32.5	49.70	50.12	50.48	50.95	51.82
35.0	49.44	49.89	50.22	50.68	51.62
37.5	49.18	49.64	50.09	50.54	51.43
40.0	48.92	49.38	49.84	50.27	51.24
45.0	48.52	-	49.45	49.87	50.83
50.0	-	-	48.95	49.36	50.43
55.0	-	-	48.58	49.09	50.15
60.0	-	-	48.32	48.82	50.00

Table 2. Slop (a), interception (b) and correlation factor R^2 of the lineal equation

$$\gamma = aT + b$$

System	a	b	R^2
n-hexane/water	-0.0857	52.432	0.9944
n-heptane/water	-0.0896	52.99	0.9957
n-octane/water	-0.0835	53.219	0.9969
n-nonane/water	-0.0822	53.621	0.9953
n-dodecane/water	-0.0757	54.333	0.9930

Table 3. Comparison between interfacial tension values calculated in this work and those reported by Goebel and Lukenheimen[4]

System	$\gamma(1)$/mN.m^{-1} this work	$\gamma(2)$/mN.m^{-1} literature	$\Delta\gamma=\gamma(1)-\gamma(2)$ (mN/m)
n-hexane/water	50.55	51.4	-0.85
n-heptane/water	51.02	51.9	-0.88
n-octane/water	51.38	52.5	-1.12
n-nonane/water	51.81	52.4	-0.59
n-dodecane/water	52.67	53.7	-1.03

FIGURE CAPTIONS

Figure 1. Pendant drop showing the geometrical variables.

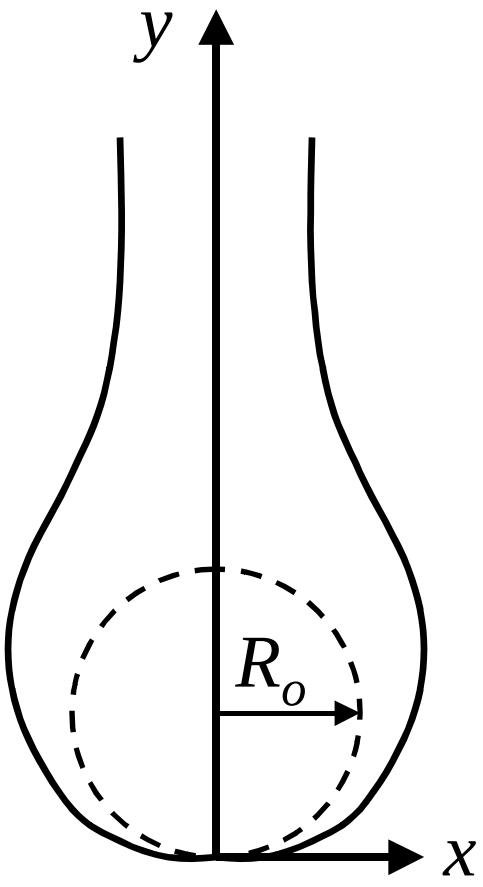
Figure 2 Experimental set-up of the equipment used to obtain TGA images from pendant drops (1: Video camera, 2: Lenses, 3: visualization cell, 4: syringe, 5: diffuser, 6: fiber optic lamp, 8: high resolution monitor, 9: video recorder and 10: computer with TARGA).

Figure 3 Original image (TARGA format) for pendant drop.

Figure 4. Pendant drop image after the computer image analysis. (a) Black and white image. (b) Drop outline.

Figure 5. Interfacial tension values as a function of temperature for several n-alkanes

Figure 6. Interfacial tension calculated from the correlation proposed in this work (2) as a function of interfacial tension experimental values (1).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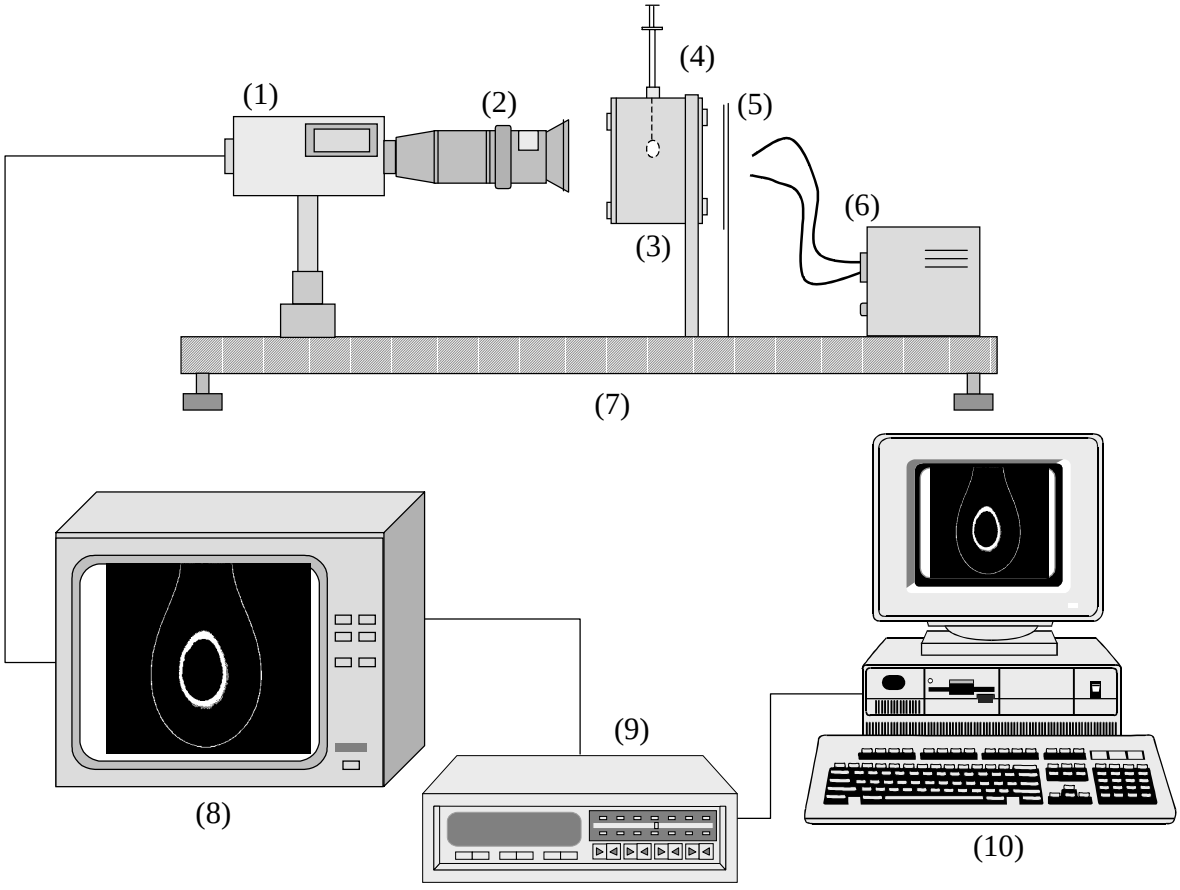
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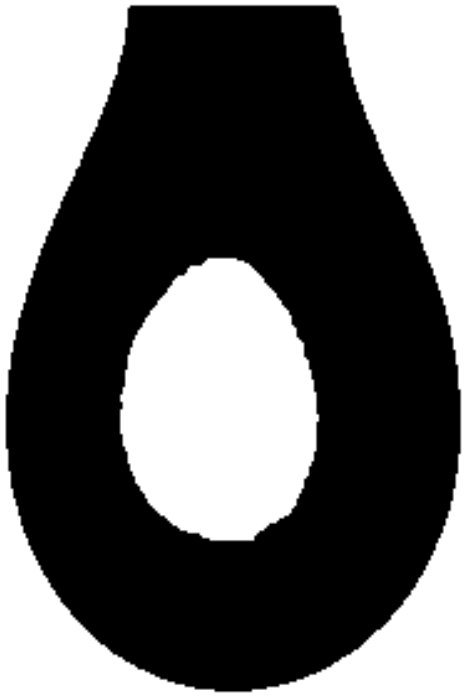

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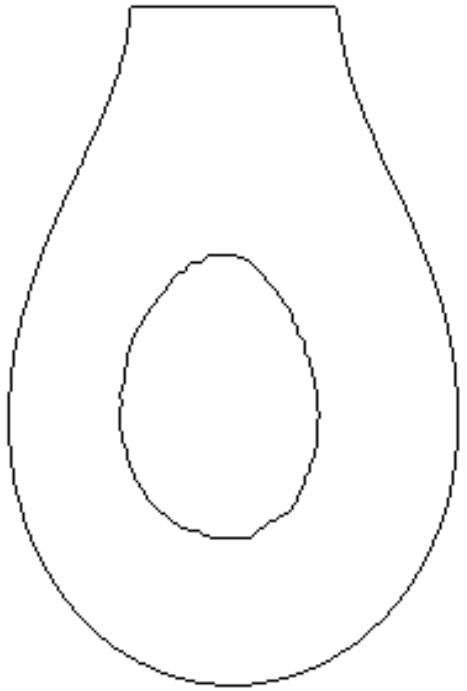

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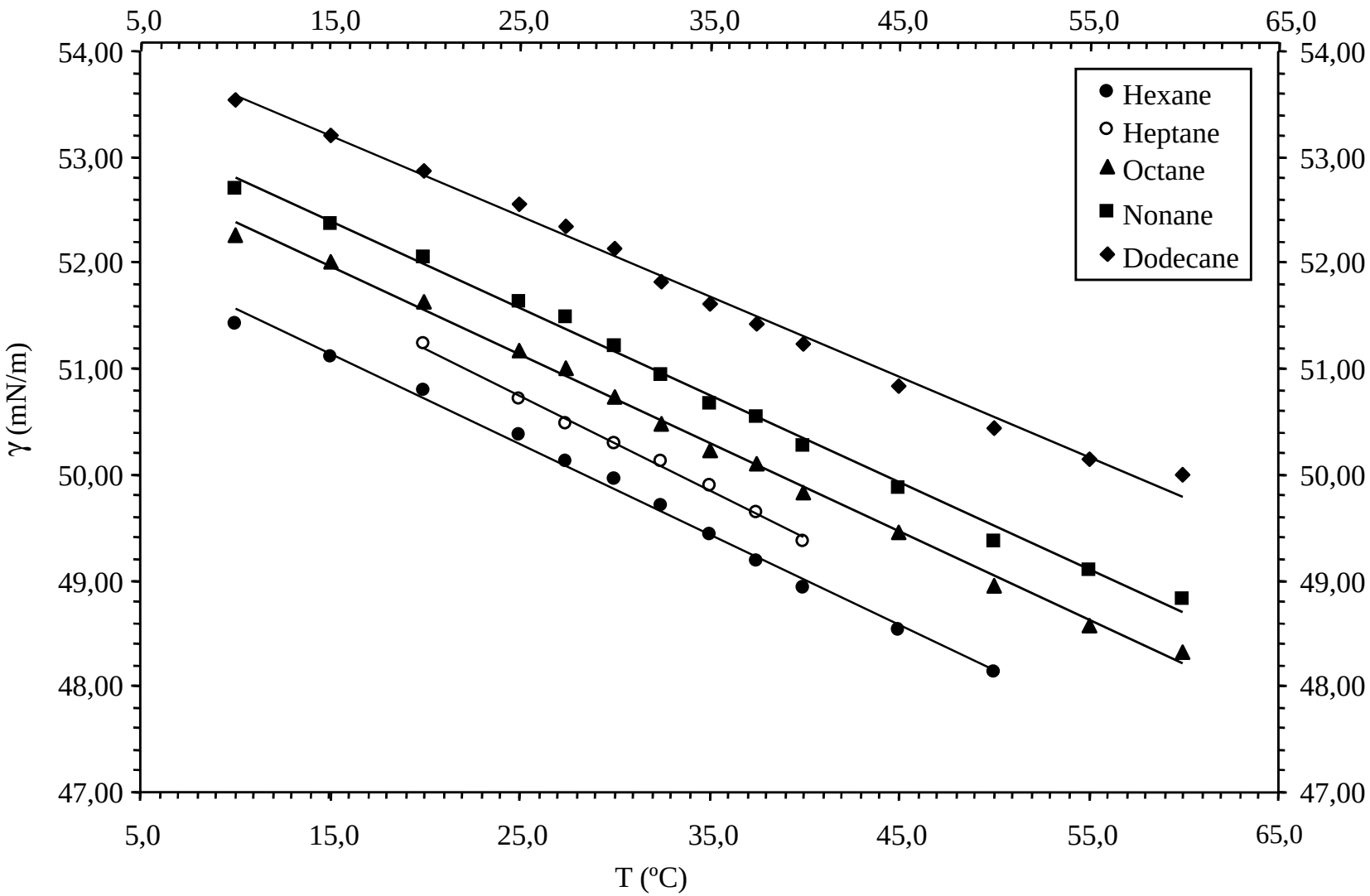
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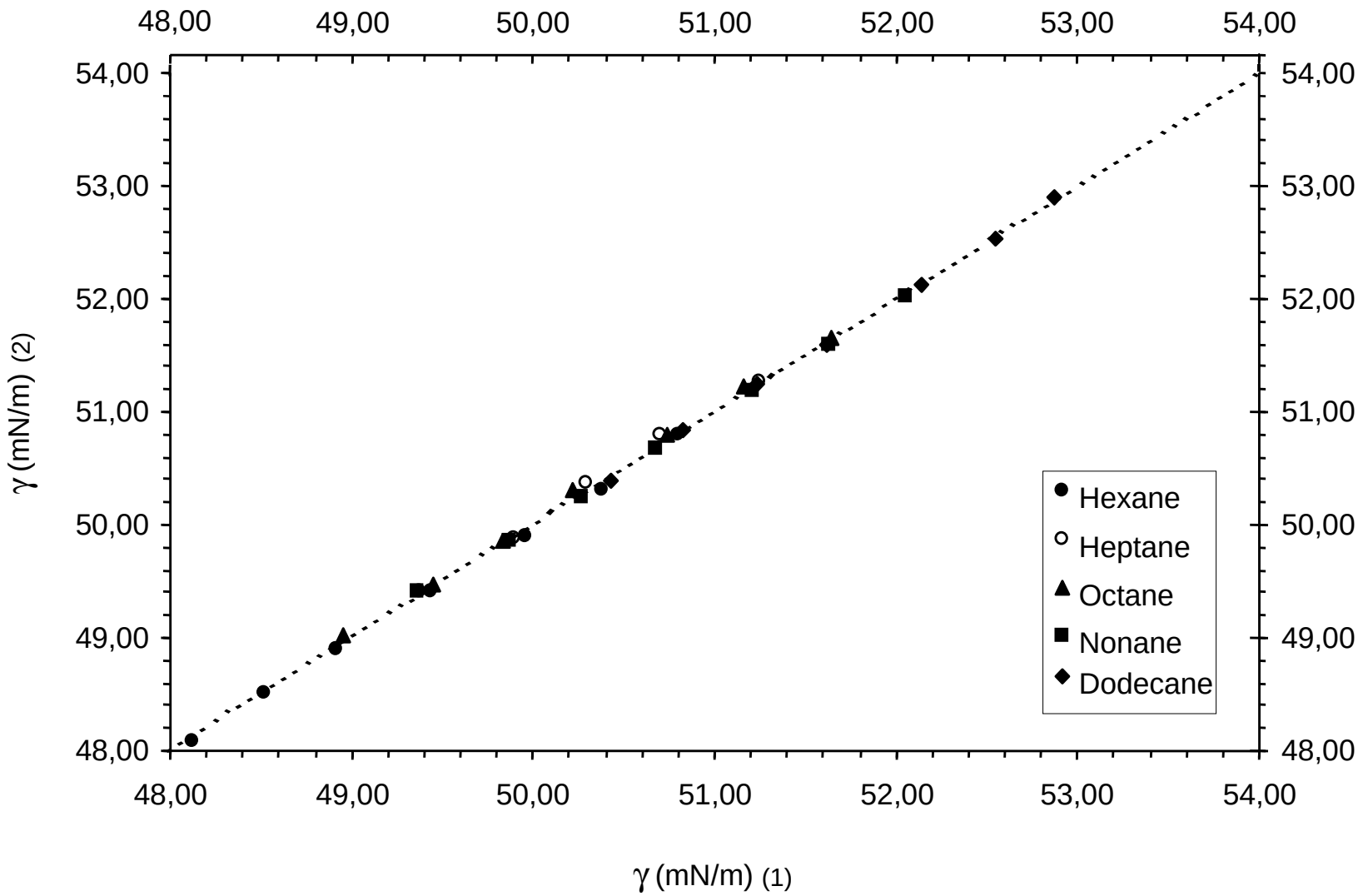
γ (mN/m)
T (ºC)
Hexane
Heptane
Octane
Nonane
Dodecane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γ (mN/m) (2)
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Heptane
Octane
Nonane
Dodecane